Supporting Information

Understanding Nonlinear Optical Phenomena in N-Pyrimidinyl Stilbazolium Crystals via a Self-Consistent Electrostatic Embedding – DFT Approach

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Table S1. CAM-B3LYP results for the static linear and nonlinear optical properties of the OPR-based crystals obtained with the 6-311++G(d,p) and 6-311G(d,p) basis set.

Basis set	OPR-CBS (isolated)	OPR-CBS (embedded)	OPR-T (isolated)	OPR-T (embedded)	OPR-VBS (isolated)	OPR-VBS (embedded)
			$\langle\alpha\rangle$ (in 10^{-24}esu)			
6-311++G(d,p)	56.48	58.75	55.21	56.23	58.24	58.94
6-311G(d,p)	52.73	54.76	51.74	52.56	54.45	54.93
			β_{tot} (in 10^{-30}esu)			
6-311++G(d,p)	179.45	233.12	170.19	196.63	180.82	211.96
6-311G(d,p)	175.18	223.71	166.31	190.25	177.45	205.57
			β_{zzz} (in 10^{-30}esu)			
6-311++G(d,p)	44.24	19.56	25.01	8.45	36.74	13.58
6-311G(d,p)	41.63	16.48	23.55	6.94	34.49	11.53
			β_{yyy} (in 10^{-30}esu)			
6-311++G(d,p)	-82.48	-166.97	-103.54	-165.40	-91.43	-156.83
6-311G(d,p)	-82.75	-163.46	-103.48	-162.25	-92.82	-154.77
			$\langle\gamma_{\parallel}\rangle$ (in 10^{-36}esu)			
6-311++G(d,p)	294.42	343.14	293.75	316.57	332.05	367.26
6-311G(d,p)	261.23	291.54	263.06	275.92	295.18	322.18

Table S2. CAM-B3LYP results for vector components of ground-state dipole moment ($\vec{\mu}_{gg}$), excited-state dipole moment ($\vec{\mu}_{ee}$) and transition dipole moment ($\vec{\mu}_{ge}$) of the OPR crystals. All values are given in D.

Crystal	$\mu_{gg,x}$	$\mu_{gg,y}$	$\mu_{gg,z}$	$\mu_{ee,x}$	$\mu_{ee,y}$	$\mu_{ee,z}$	$\mu_{ge,x}$	$\mu_{ge,y}$	$\mu_{ge,z}$
OPR-CBS	11.531	-2.812	14.610	8.418	5.200	13.155	-3.349	10.016	-0.819
OPR-T	11.531	-2.812	14.610	8.418	5.200	13.155	-2.637	9.938	-0.807
OPR-VBS	10.918	-1.515	14.142	4.554	6.408	8.893	-3.188	8.312	-0.564

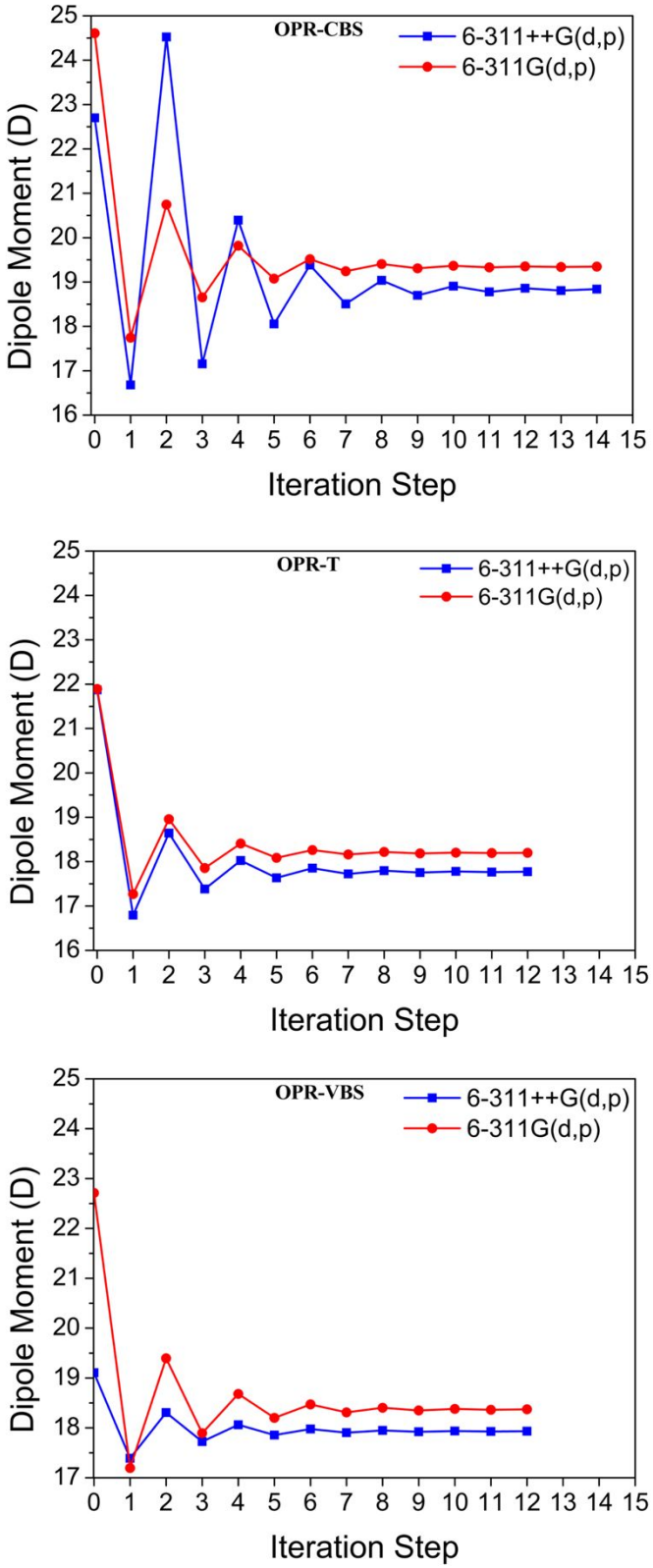

Figure S1. Convergence of dipole moment of the OPR-based crystals as function of the iterative procedure.

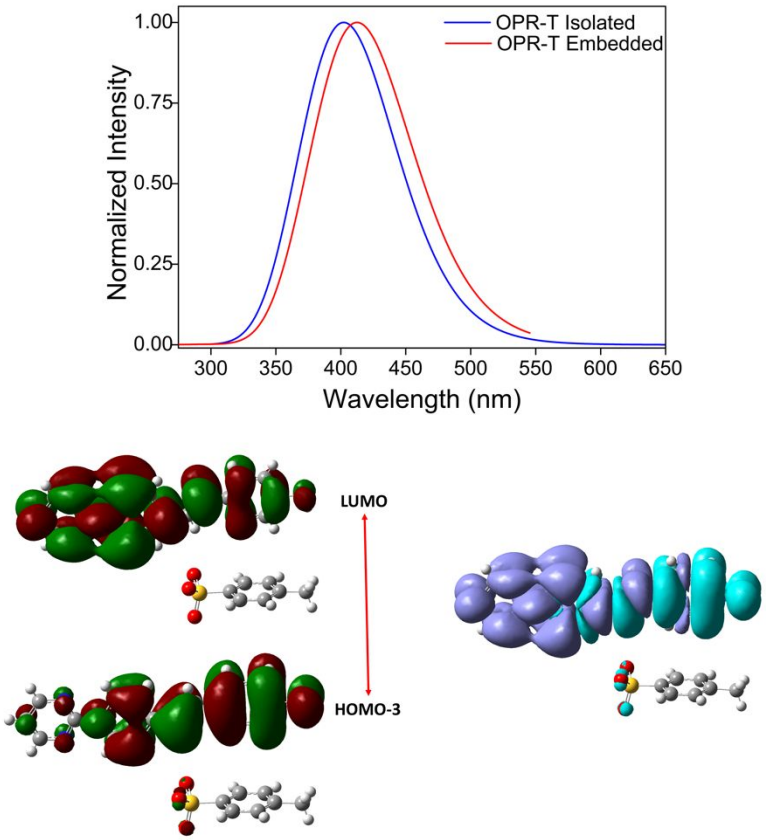

Figure S2. Theoretical UV–Vis absorption spectra of unit cell of OPR-T crystal. Gaussian convolution a with full width at half maximum (FWHM) of 0.3 eV. Frontier orbitals involved in the dominant transition and change in electron density. The aqua blue (purple) color indicates the region where the electrons are coming (arriving).

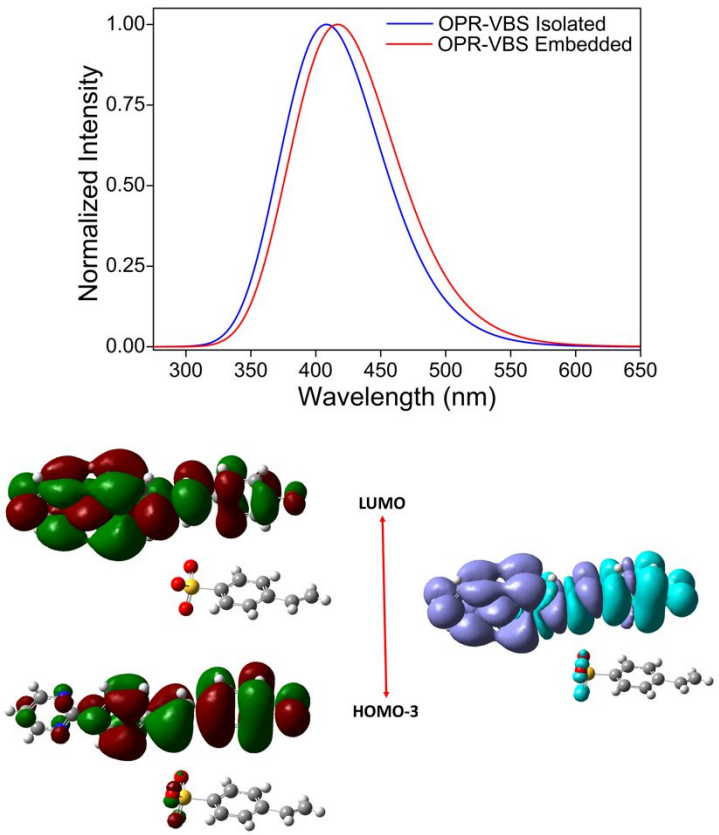

Figure S3. Theoretical UV–Vis absorption spectra of unit cell of OPR-VBS crystal. Gaussian convolution a with full width at half maximum (FWHM) of 0.3 eV. Frontier orbitals involved in the dominant transition and change in electron density. The aqua blue (purple) color indicates the region where the electrons are coming (arriving).